



Synthesis and Characterisation of complexes of Cu(II) Containing macrocyclic ligand

Mahesh Kumar, Dept. of Chem.
M.M College Bhagalpur
Biswajit Kumar Biswas
At-Goalgaon, Po-Shikarpur,
Dist-Uttar Dinajpur, (W.B.) 733201

Abstract: The field of organometallic chemistry of transition metal is developing very fast because of its variety of application and importance in the area of coordination chemistry.

In the past, attention has been paid on the design and the synthesis of organometallic compound containing macrocyclic ligand.

The copper complexes containing cyclic ligands in octahedral geometry are very important and its biological activities have great importance. Biological importance of macrocyclic ligand is important but there complexes of macrocyclic ligand has great importance.

(Key Words) : Macrocyclic ligand (DAMSC), H₂(dial), diamino benzene, butanal)

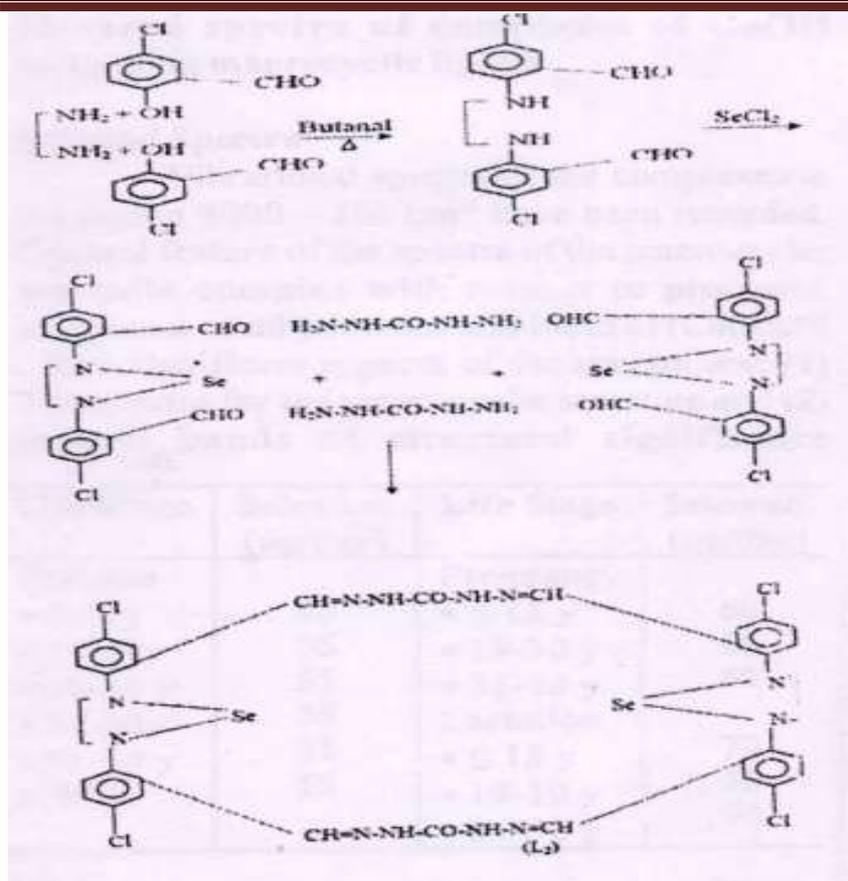
Introduction

Macrocyclic Complexes of metal ligands have numerous application in biological field metal complexes of macrocyclic ligand containing Se and N-donor atoms are known and possess antimicrobial, antiviral, antifungal, anticancerous activities. The metal complexes just look like Schiff's Base.

The present paper discussed the synthesis and characterization of Cu(II) and DAMSC.

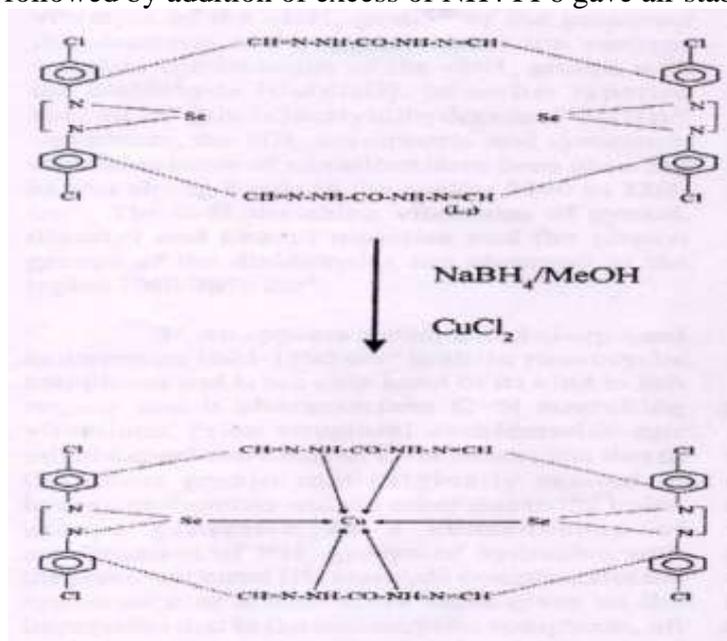
Synthesis of Ligand (Preparation of H₂ dial)L₂

A solution of 5 chlorosalicylaldehyde (31.1g, 0.2mol) in DAMSC (120 ml) was added to a 200 ml aqueous solution of sodium hydroxide (8g, 0.2mol) and the mixture was warmed. The warmed solution was treated with 1,2 diaminoethane (6.0g, 0.1 mol) in DAMSC (120ml). The resulting solution was refluxed under nitrogen for about 12 h and was allowed to stand at 0°C. Cream coloured crystals were formed which were recovered and washed with water, recrystallization was done from an ether chloroform mixture. The yield is about 40%. The synthetic reaction can be shown below :-



Synthesis of metal complexes

The reaction of 1 mole CuCl_2 with 1 mole of above ligand(L_2) is refluxing with methanol followed by addition of excess of $\text{NH}_4 \text{PF}_6$ gave air stable complexes



Therapeutic Aspect :

Medicinal Uses :

1. Due to its anit-seborrhics ,antikeraolytics properties selenium , sulphide as a2.5% lotion or shampoo is used as an anti-dandruff shampoo.
2. Due to its antioxidant properties selenium dioxide (200ug) and selenomethionine(60-100ug) is used in antioxidant formuation.
3. Selenium (150ug) is used as a prophylactic and therapeutic agent for free for radical madeated disorders like : CAD, premature ageing, cataract etc.

Selenium Deficient Disease :

- 1.Keshandisease or cardiomyopathy.
- 2.Kaschinbeck disease or endemic human osteopathy.
3. Hyperthyroidism

Recommended Dietary Allowances

Results and Discussion

Infrared Spectra of complexes of Cu(II) containing macrocyclic ligand

Infrared Spectra

Vibrational spectra of the complexes in the region 4000-300cm⁻¹ have been recorded.General features of spectra of the macrocycles are quite complex with respect to precursor complexes of dihydrazone and those of [Cu(dial)]. Two significant aspects of the spectra are : (1) The spectra for the macrocyclic structure and (2) several bands of structural significance

Life Stage	Selenium (µg/day)						
Infants		Males		Females		Pregnancy	
• 0-6 mo	15	• 9-13y	40	• 9-13y	40	• ≤ 18 y	60
• 7-12 mo	20	• 14-18y	55	• 14-18y	55	• 19-30 y	60
Children		• 19-30 y	55	• 19-30 y	55	• 31-50 y	60
• 1-3 y	20	• 31-50y	55	• 31-50y	55	Lactation	
• 4-8y	30	• 51-70 y	55	• 51-70 y	55	• ≤ 18 y	70
		• > 70 y	55	> 70 y	55	• 19-30 y	70
						• 31-50 y	70

Characteristics of the precursors have disappeared from the spectra of the macrocycles because of Schiff base condensation.

There is no band in the region 3300-3100 cm⁻¹ which can be assigned to the stretching vibration of the -NH₂ groups of the precursor dihydrazones and suggests metal ion assisted template condensation of the -NH₂ groups with the dialdehyde [Cu(dial)]. In earlier reported spectra of [bis-(diacetyldihydrazone) M(II)]₂+ complexes, the NH₂ asymmetric and symmetric stretching mode of vibrations have been observed as two strong bands in the region 3300 to 3200 cm⁻¹. The C-H stretching vibrations of glyoxal, groups of the dialdehydes are observed in the region 3060-2870cm⁻¹.

There appears a strong and sharp band 1605-1590cm⁻¹ in all the macrocyclic complexes and is the only band of its kind in this region and it characterizes C=N



stretching vibrations. From structural consideration one might expect two kinds of C=N bands, one due to the imine groups are nearly of the same vibrational energies which arises due to high degree of conjugation or electron delocalization in the resultant macrocyclic structure.

A pair of bands which clearly recognizable and have the characteristics features observed in the spectra of the dialdehydes are located at 1240-1225 cm^{-1} and at 1060-1040 cm^{-1} respectively. These are asymmetric and symmetric ethereal C-O-C stretching vibrations. From energy considerations they appear at a relatively lower frequency region in the macrocyclic complexes compared to the corresponding vibration observed for the free dialdehydes and the lowering of energy can be directly attributed to involvement of ethereal oxygen atoms in coordination with metal centers.

Several other vibrational bands which self consistent with stretching vibrations of the macrocyclic skeleton are also observed in the infrared spectra of the complexes. The first group of bands is observed near 1480 and 1280 cm^{-1} . They arise due to skeletal vibrations of the phenyl and ethyl groups and deformation mode of vibrations of -CH₃ and -CH₂ groups of the appropriate macrocycles. In the lower energy region 900-600 cm^{-1} there also appear a few bands which may be assigned to the effect of substitution on the phenyl rings and other skeletal modes of vibrations. The vibrational spectra as a whole satisfy the macrocyclic structures of the metal complexes of Cu(II).

Electronic spectra and magnetic properties :

In order to elucidate the structural problems, electronic spectra (Table-1 and 2) of the precursors and tricyclomacrocyclic complex were recorded respectively on Shimadzu 160A and Beckman-20 spectrophotometers. The model-303 and Guoy balance respectively. Low value of molar conductivity in the range 10-15 $\text{cm}^2 \text{mol}^{-1}$ indicates the precursor and macrocyclic complex to be non-electrolytic in nature. The magnetic moment of macrocyclic precursors [Cu(C₄₂H₂₈N₁₂)Se₂] indicate to be diamagnetic. Electronic spectrum with a broad band with low intensity at 20000 cm^{-1} suggests the stereochemistry to be square planar. Non-macrocyclic precursors [Cu(C₄₂H₂₈N₁₂)Se₂] have μ_{eff} in the ranges 3.12-3.22 B.M. indicating them to be octahedral in nature. The electronic spectra are also in good agreement with the literature.

For the present groups of macrocyclic complexes, the parameters D and D which represent the crystal field strength of the macrocyclic ligands and the metal-ligands interaction (of Cl ion) along the axial direction remain practically constant. The ligand field parameters have comparable magnitudes with the corresponding D and D values for the chloro complexes of cobalt(II) with 1,2-diphenylethane-1,1'-diylhydrazine. The near constancy of the parameters along the series indicates that the metal-ligand interaction along the axial direction and in the plane do not mutually influence each other. It may be pointed out that the results for the tetragonal cobalt(II) complexes show that the D parameter is practically invariant for the similar [Cu(Py)₄X₂] complexes (Py is pyridine and X is a halide ion) and the ligand field effects are not transferable.

But in the case of some carboxylate complexes, the parameter D is found to be affected with the carboxylate group and the effect has been attributed to the transferability of the ligand field effects.

The electronic spectra and magnetic susceptibility show that the nickel ions are present in two types of stereo chemical environments. The central nickel ion ion is octahedrally coordinated. It seems that a pair of Cl ions is bonded to central Cu(II) ion.

TABLE 1
Electronic Spectral Bands (in Cm^{-1}) and magnetic moments (in B.M.) of the Cu(II) macrocyclic complexes.

Complexes	${}^3B_{1g} \rightarrow {}^3E_g$	${}^4B_{2g}$	${}^3T_{1g}$	${}^3T_{1g}(P)+C.T.$	C.T.	$\mu_{\text{eff}}/\text{metal ion}$
[CuMe ¹ Cl ₂]	7600	11500	16000	28000	-	2.80
[CuMe ² Cl ₂]	7700	11400	19000	28000	-	2.99
[CuMe ³ Cl ₂]	7500	10500	16500	28500	42000	2.90
[CuMe ⁴ Cl ₂]	7800	11100	18200	28500	42300	2.91
[CuMe ⁵ Cl ₂]	7400	10200	18000	28000	-	2.95
[CuMe ⁶ Cl ₂]	7500	11500	18300	28500	-	2.95
[CuMe ⁷ Cl ₂]	7300	10400	18200	28000	-	2.80
[CuMe ⁸ Cl ₂]	7400	10800	18100	27500	-	2.90

Table-2
Calculated Electronic Spectral Parameters (cm^{-1}) for the trinuclear Cu (II) macrocyclic complexes.

Complexes	D_1	D_2^{xy}	D_3^z
[CuMe ¹ Cl ₂]	372	1190	720
[CuMe ² Cl ₂]	361	1180	740
[CuMe ³ Cl ₂]	336	1090	750
[CuMe ⁴ Cl ₂]	382	1170	700
[CuMe ⁵ Cl ₂]	349	1040	730
[CuMe ⁶ Cl ₂]	384	1110	700
[CuMe ⁷ Cl ₂]	359	1040	720
[CuMe ⁸ Cl ₂]	390	1065	725

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